Research proposal

For the registration for Ph.D. Program in Chemistry, Faculty of Science,

Swami RamanandTeerth Marathwada University, Nanded

"Studies on Optical, Structural & Kinetic Properties of Chromium (VI) Complexes

By

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Research Guide

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Introduction :-

Oxidation reactions are very important in nature and in organic synthesis. Among the most important oxidizing agents, chromium(VI) Halochromates have been used as mild and selective oxidizing agents for many types of substrates varying from metal ions to naturally occurring organic compounds and have wide range of applications in synthetic chemistry .

A variety of Compounds containing chromium (VI) have proved to be versatile reagent capable of oxidizing almost every oxidizing functional group. Chromium exists in both trivalent Cr (III) and hexavalent Cr (VI) species in aqueous solution and the two oxidation states are identified by various physical & Chemical properties . chromium (VI) compounds are found toxic & very dangerous for biological systems, while chromium (III) are relatively non – toxic[1]

The chemistry of chromium (V) and chromium (IV) as an intermediate species which may be formed during the reduction of chromium (VI) were attracted by many researchers because of their involvement in the Mechanism of Cr-induced cancers [2]

A number of new chromium containing compounds like pyridinium bromochromate[3], quinolinium chlorochromate[4] 2,2'bipyridinium chlorochromate[5], pyridinium flurochromate[6] quinolinium flurochromate[7], quinolinium bromochromate[8] , quinolinium dichromate[9], pyridinium flurochromate[10], imidazolium flurochromate[11] have been used to study the kinetics & and mechanism of oxidation/bromination of various organic compounds.

However, most of reagents developed so far suffer from atleast one of the drawbacks such as high acidity, photosensitivity, hygroscopy , low selectivity, long reaction time and need for large excess of reagent. To overcome these disadvantages, we are trying to synthesize new halochromates as a mild, efficient & stable reagents which are able to work as both an oxidizing agent as well as brominating agents

Objectives :-

1) Synthesis of new chromium (VI) complexes ,
2) Their Characterization ,
3) Studies on their optical properties ,
4) kinetic properties ; and
5) kinetic rate laws & mechanism of the reactions (oxidation / bromination) under study .

Methodology :-

All the chemicals and reagents are of analytical grade .

The new halo chromates will be synthesized by using the same method reported in Literature [7,8]

Optical properties , conductance measurement can be done with 1 mole of these complexes .

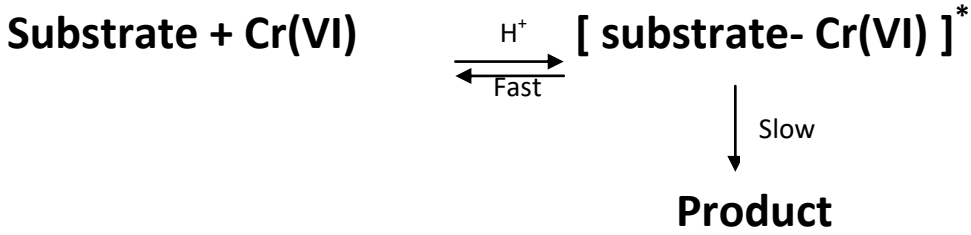
Lambert-Beer's law will be tested for these Cr(VI) complexes & intresting to know upto what concentration limit it is valid & also molar extinction coefficient , ε

Kinetic measurements can be done under pseudo – first order conditions by keeping an excess of substrate over Cr(VI) . The reaction is followed by decrease of concentration of Cr(VI) spectrophotometrically or iodometrically for 80-85% completion of reactions . The rate constant will be determined by least-square method from linear plots of log [Cr(VI)] v_s time .

The stichiometry of reaction is determined by carrying out several sets of experiments with varying amount of Cr(VI) reagents . To study the mechanism of reactions & to write the rate law , it will be studied with respect to

1. Effect of variation of [substrate] ,
2. Effect of variation of [Cr(VI)] ,
3. Effect of variation of [H^+] ,
4. Effect of variation of ionic strength ,
5. Effect of variation of solvent composition ; &
6. Effect of variation of temperature

Apart from all these , energy-entropy relationship , Exner plot , Hammet equation & determination of thermodynamic parameters can be studied to support the mechanism of reactions . Literature survey reveals the following mechanism :



Products will be confirmed by M.P , B.P , TLC & spectral analysis .

Plan of Research:- 1st Year :- Literature Survey, Reference work, Synthesis of new cr (VI) complexes, characterization by IR, NMR , Mass and elemental analysis.

2nd Year :- Studies on Physicochemical , optical Properties and also verification of Lambert – Beer Law for these complexes to find out , ε .

3rd Year :- Kinetics and mechanistic Study of hydrocarbons , amino acids as well as substituted hydroxyl aromatic compounds by these reagents .

Scope of the work :- There is a wide scope in synthesis of complexes with chromium (VI) as central atom for oxidation of aromatic compounds as mild, efficient and stable reagents.

Some of reagents are acting as brominating agents which may be an alternative to bromine which is hazardous and poisonous

During the kinetic study , Cr(VI) changes to Cr(IV) .

Reactions are carried out by 50% acetic acid (v/v) in presence of $[H^+]$ ions & rate of reaction may be dependent of $[H^+]$ ions ; i.e. acid-catalysed reactions .

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